

IGNITION ACTIVATION ENERGY OF MATERIALS BASED ON POLYAMIDE 6

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Research article

Abstract: This contribution is aimed to compare the values of the ignition activation energies of two types of polyamide – Slovamid 6 FRB and Slovamid GF 50 LTS. Samples were isothermally stressed at five different temperatures between 500 °C a 550 °C, while the time to initiation of the flame combustion was monitored. Subsequently from the measured times were compiled Arrhenius plots under which activation energy of ignition of both polymers were calculated. The values of activation energies were 106 kJ.mol⁻¹ and 158.0 kJ.mol⁻¹ for Slovamid 6 FRB 4 and Slovamid 6 GF 50 LTS.

Keywords: Activation energy, Ignition, Polyamide 6, Thermal decomposition, Time to ignition.

Introduction

Aliphatic polyamides are important engineering resins manufactured in large quantities for fibre, film and plastic applications. Polyamide 6 (PA6) together with polyamide 6.6 (PA6.6) are produced in the largest volume, whereas polyamides 7, 11, 12, 4.6, 6.10 and 6.12 are speciality products with significantly lower volumes of production. Depending on the method used, the sample heating rate and the air flow, the ignition temperatures for polyamides were found in the range 370 °C – 540 °C. (Levchik and Weil, 2000)

Thermogravimetric analysis showed that polyamides based on renewable resources (named bio-polyamides) decompose in one step in inert atmosphere and in three steps in oxidative conditions. In inert atmosphere a wide range of compounds was found to be produced during the thermal degradation with a few steps of evolution. Except of the low molecular weight volatiles, like H₂O, CO, CO₂ and NH₃, aliphatic compounds, terminal vinyl groups, cyclic compounds and long chain alkenes were detected. Under oxidative atmosphere, the major products of degradation were carbon monoxide, carbon dioxide, water and ammonia. (Pagacz et al., 2015) Similar results were also mentioned by

Herrera et al. (2001) According to their results the polyamides decompose apparently in one step in nitrogen and in two steps in air, but a detailed study confirmed that the decomposition has two steps in nitrogen and at least three steps in air. The extra step in air is due to the degradation of the char formed in the first step.

PA6 is extensively used in engineering applications because of its unique characteristics such as low price, low viscosity, high toughness, shelf lubricating behaviour and high chemical resistance. (Pashaei et al., 2011) It belongs to flammable material with a low limiting oxygen index (LOI) value (about 21 %) and severe flammable dripping, which inhibit the further application of PA6 in many fields. (Ge et al., 2015; Novozhilov et al., 2011)

During thermogravimetric testing of PA6 in nitrogen atmosphere it was determined that the decomposition of PA6 in inert atmosphere (nitrogen gas flow of 60 mL.min⁻¹) occurs in the range of 345 °C – 511 °C with one DTG peak at 472 °C. (Pashaei et al., 2011) The TGA a DTG curves are shown in Fig. 1.

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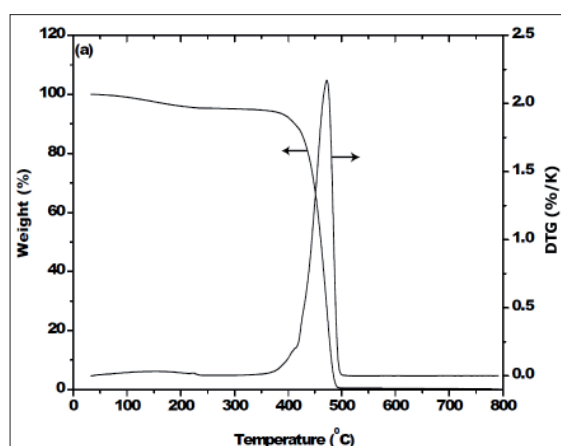


Fig. 1 TGA and derivative thermogram of PA6 heated at rate of 20 °C.min⁻¹ in nitrogen stream (Pashaei et al., 2011)

During the testing on cone calorimeter, the ignition time of the PA6 (exposed horizontally to an external heat flux of 35 kW.m⁻²) was 105 s, and the peak value of HRR was 1064 kW.m⁻², the peak value of mass loss rate was 0.252 g.m⁻².s⁻¹. (Du et al., 2007) Novozhilov et al. (2011) claim that at an external heat flux of 60 kW.m⁻² the peak value of HRR was 863 kW.m⁻².

The combustion products of PA6 contained compounds with diverse structures, whereas non-flaming combustion yielded a relatively small overall amount of volatile product. The combustion products comprise primarily nitrogen-containing compounds and no oxygen-containing oxidation products other than CO and CO₂. (Levchik and Weil, 2000) Bockhorn et al. (1999) claim that the main decomposition product of PA6 in helium flow at heating rate of 2 K.min⁻¹ is ϵ -caprolactam (92 %). Identified by-products analysed by GC/MS are the cyclic dimer, i.e. 1,8-diazacyclotetradecane-2,9-dione (4 %), 5-hexene acid amide (2 %), 5-hexen nitrile (1 %), hexane nitrile (0.5 %) and 2-cyclohexen-1-one (0.5 %). The toxicity of thermal decomposition products of PA6 is mentioned in the work of Esposito and Alarie (1988).

The weight loss of pure PA6 takes place in a single step with a maximum rate of weight loss at 459 °C, and the char residue is 2.7 % at 700 °C (Ge et al., 2015), but the thermal degradation of PA6 involves the following processes:

1. an intramolecular backbiting process and
2. hydrogen transfer reaction leading to scission of the C-N bond β to the amide group. (Kutz, 2005)

The energy barrier opposing the reaction is named activation energy. (Kissinger, 1956) Activation energy of thermal decomposition of polyamides was studied in several works (Tab. 1).

Tab. 1 Activation energies of various polyamides at different conditions

Material	Atmosphere	Activation energy	Source
PA6	N ₂	111–276	(Du et al., 2007)
PA6	N ₂	264	(Du et al., 2007)
PA6	N ₂	276	(Du et al., 2007)
Nylon	vacuum	232	(Nelson, 1967)
Nylon	vacuum	200	(Nelson, 1967)
Nylon	vacuum	154	(Nelson, 1967)
Nylon	vacuum	155	(Nelson, 1967)
Nylon	vacuum	216	(Nelson, 1967)
PA6	Nitrogen	162	(Herrera et al., 2001)
PA6	Nitrogen	476	(Herrera et al., 2001)
PA66	Nitrogen	91	(Herrera et al., 2001)
PA66	Nitrogen	310	(Herrera et al., 2001)
PA12	Nitrogen	2208	(Herrera et al., 2001)
PA12	Nitrogen	260	(Herrera et al., 2001)
PA612	Nitrogen	164	(Herrera et al., 2001)
PA612	Nitrogen	400	(Herrera et al., 2001)
PA6	Air	153	(Li et al., 2006)

Materials and methods

Granulated samples of Slovamid 6 FRB 4 and Slovamid 6 GF 50 LTS were tested in this experiment. In both cases it was a material based on PA6, while the first mentioned contained fire retardants on non-halogenated bases for injection molding. Designed for the electrotechnical industry (good flow properties and good resistance to injection faults. Suitable for thin-walled products and wide area cable boxes. (Plastcom, 2013a)

Slovamid 6 GF 50 LTS is PA6 reinforced with 50 % glass fiber with UV and heat stabilizers for injection molding. It is used for the production of tough and high strength products in the automotive, electrical, engineering and consumer industry (holders for electric tools, hobby tools, gear units, fan parts etc.). (Plastcom, 2013b)

Comparison of the basic properties of the two materials is shown in the Tab. 2.

Tab. 2 Basic properties of the tested polymers (Plastcom, 2013a; Plastcom, 2013b)

	Slovamid 6 FRB 4	Slovamid 6 GF 50 LTS
Density [kg.m ⁻³]	1190	1550
Melting temperature [°C]	220	220
Glow-wire flammability index [°C]	960	650
Moisture content [%]	0.15	0.15

For each polyamide five samples were tested polyamides. Statistical evaluation of the weights is shown in Fig. 2. As apparent, the deviations from the average weights of the samples were less than 1 %, while for sample of SLOVAMID 6 GF 50 LTS the variance was minor.

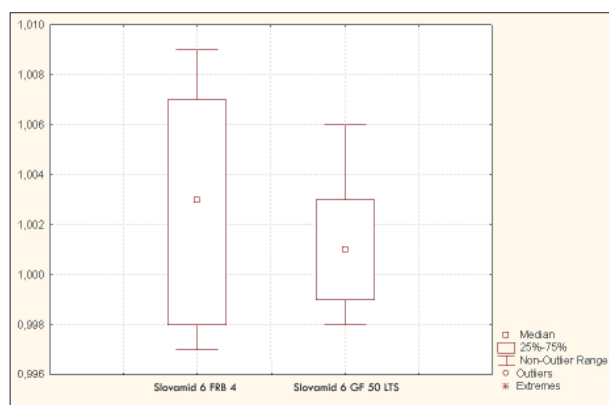


Fig. 2 Weight box plot of tested samples

To maintain the isothermal conditions hot-air furnace with a control unit CLARE 4 was used, complying with standards ISO 871 (2010). The measurements were conducted in a stream of air. Both types of material were successively exposed to a temperature of 500 °C, resp. 510 °C to 540 °C, resp. 550 °C. At every temperature a time to initiation of flame combustion was monitored.

Kinetic theory

The dependence of the temperature and reaction rate describes the Arrhenius law, according to which the kinetics of a chemical reaction can be described as follows:

$$k = A \cdot e^{-\frac{E_A}{R \cdot T}} \quad (1)$$

where k is the rate constant, A is the frequency factor, E_A is the activation energy, R is the universal gas constant and T is the absolute temperature. Logarithm of equation (1) gives a linear relationship:

$$\ln k = \ln A - \frac{E_A}{RT} \quad (2)$$

Semenov (1959) in his work deduced that in the case of characterizing reaction rate of ignition by the time to ignition of the sample under isothermal heating the relation (2) can be written as:

$$\ln t_i = \ln A - \frac{E_A}{RT} \quad (3)$$

where t_i is the time to ignition of the sample. If the ignition activation energy is considered as a constant characteristic of the material, it is possible to determine the dependence of the natural logarithm of time to ignition from the inverse value of the thermodynamic temperature of the heating during several temperature measurements. If the slope of mentioned dependence is labeled b then the following applies:

$$E_A = -b \cdot R \quad (4)$$

This method of calculation was mentioned by for example Martinka et al. (2015) and Balog, Tureková and Slabá (2005).

Results and discussion

The measured initiation times of the samples at various temperatures are shown in Tab. 3. These values indicate that it is a logarithmic dependence, corresponding to the general equation (3).

Tab. 3 Time to ignition of the samples as a function of the ambient temperature

Slovamid 6 FRB 4		Slovamid 6 GF 50 LTS	
Temperature [°C]	Time to ignition [s]	Temperature [°C]	Time to ignition [s]
500	103	510	120
510	86	520	89
520	66	530	69
530	52	540	49
540	48	550	37

From the measured values of the time to ignition of the samples and their corresponding temperatures (Tab. 3), dependence of the natural logarithm of the induction period from the inverse value of the thermodynamic temperature was created. Trend line was covered by the points of this dependence and the slope was inserted into the equation (4). Subsequently, for each of the polymer an activation energy of ignition was calculated. Mentioned dependencies are shown in Fig. 3 and 4.

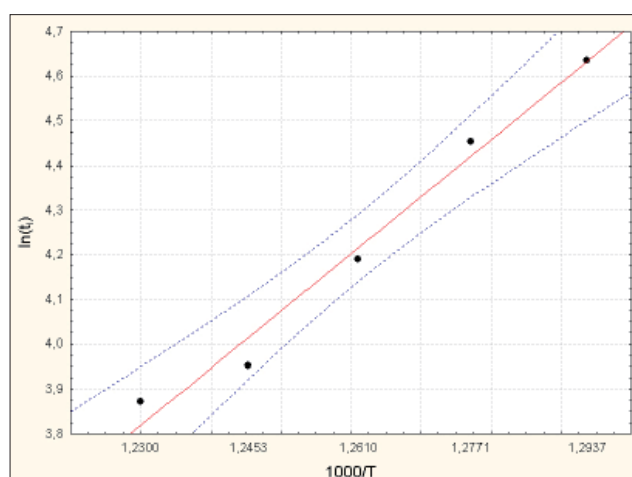


Fig. 3 Arrhenius plot of Slovamid 6 FRB 4

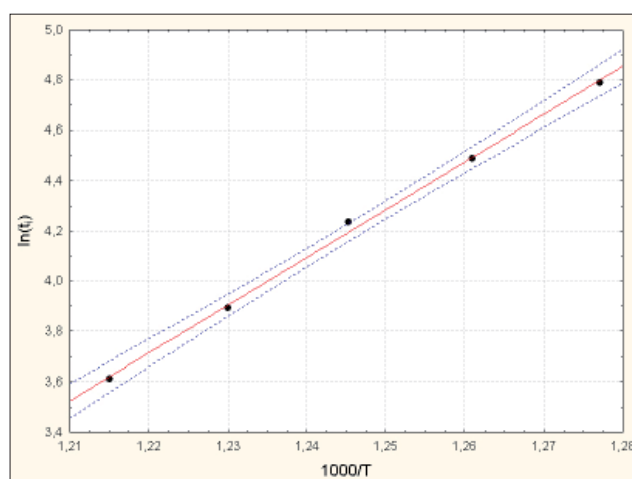


Fig. 4 Arrhenius plot of Slovamid 6 GF 50 LTS

Regression strips flanking the double-sided 95 % confidence interval are shown in both figures. The square of the correlation coefficient for Slovamid 6 FRB 4 is slightly lower, but still achieves significantly high levels of 0.9798. Slovamid 6 GF

50 LTS achieves even stronger correlation with R^2 equal to 0.9978.

As mentioned above, the activation energies were calculated from the slope of the trend lines of the particular material. The value of the ignition activation energy of Slovamid 6 FRB 4 was 106 kJ mol^{-1} . The ignition activation energy of Slovamid 6 GF 50 LTS was higher ($158.0 \text{ kJ mol}^{-1}$). If these values are compared with those given in the literature (Tab. 1), SLOVAMID 6 GF 50 LTS achieves a typical activation energy for the decomposition of pure polyamide 6 in the air mentioned by Li et al. (2006). Observation of Yin, Krifa and Koo (2015) indicates that the presence of FR additives decreases PA6 thermal stability, particularly at the onset of decomposition, what is consistent with the ignition times indicated in the Tab. 3.

Conclusion

Polymeric materials currently find a wide range of applications. This contribution aims to calculate the activation energy of ignition of two types of polyamide. Samples used in this experiment were Slovamid 6 FRB 4 and Slovamid 6 GF 50 LTS. Using a method of randomization from each material were taken samples which were subsequently heated isothermally at five different temperatures. Both polymers exhibited a time dependence from the ignition and form the inverse value of the thermodynamic temperature as a logarithmic course. The activation energy of ignition for Slovamid 6 FRB 4 was 106 kJ mol^{-1} and for Slovamid 6 GF 50 LTS it was $158.0 \text{ kJ mol}^{-1}$.

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